Study of CO_2 Absorption and Desorption in a Packed Column

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ABSTRACT

Carbon dioxide, a major greenhouse gas, may need to be removed from flue gas produced by combustion of fossil fuels in order to manage future climate changes. Although conventional wet scrubbing techniques exist for removal of carbon dioxide from gas streams, the wet scrubbing techniques must improve to process large volumes of flue gas at acceptable thermal efficiencies and minimal costs. Amine scrubbing is one such technique to remove CO_2. In order to make the process more efficient, two areas of improvement were investigated: gas-liquid contacting area and the type of reactant. Pertaining to the former, various absorption tests with conventional packing material and structured packings were conducted with mono-ethanolamine (MEA), a traditional solvent, as well as with novel amines. Significant improvements in CO_2 removal were obtained with the structured packing. With respect to the amine investigation, a key to improved efficiency is the ease of regeneration of the CO_2-loaded solvent. Testing with a sterically hindered amine, 2-amino-2-methyl-1-propanol, revealed that, although absorption was somewhat less as compared to MEA, thermal regeneration was far easier. The impact of various process parameters on the absorption and desorption steps will also be discussed.

INTRODUCTION

Chemical solvent absorption is based on reactions between CO_2 and one or more basic absorbents such as aqueous solutions of mono-, di-, or tri-ethanolamine. An advantageous characteristic of absorption is that it can be reversed by sending the CO_2-rich absorbent to a desorber (or stripper) where the temperature is raised. In the case of physical absorption, CO_2 is absorbed under pressure, and the gas desorption can be achieved at reduced pressure. The regenerated absorbent is then returned to the absorber thereby creating a continuous recycling process. The disadvantages of chemical absorption processes include their limited loadings and high energy requirements resulting from the reaction stoichiometry and the heats of absorption, respectively. There are also problems of corrosion and degradation. Physical solvents include methanol, polyethylene glycol, dimethylether, and others.

All currently available CO_2 separation processes are energy intensive. In ranking energy penalty of the processes, combustion with pure oxygen is the least energy intensive (about 30% energy penalty), and is followed by chemical solvent absorption processes (about 35% energy penalty) [2]. Also it has been concluded that even the current most efficient technology will reduce energy efficiency of utility steam plants by about 30% and will increase the price of electricity by 80%, even before disposal costs are added. These results are consistent with an EPRI study on CO_2 capture and disposal [3]. Combustion with pure oxygen requires redesign of the entire combustion and boiler system, and therefore, can not be retrofitted. The chemical solvent absorption process for CO_2 capture can be retrofitted in existing boiler systems and provides a rationale to pursue near-term evolutionary capture techniques. Emerging and future electricity generation technologies and novel CO_2 capturing methods have the potential to significantly reduce electricity costs if the control of CO_2 emissions is mandated.

EXPERIMENTAL

Absorption

Figure 1 shows a typical liquid chemical absorption process for CO_2 capture. The flowsheet represents a continuous absorption/regeneration cycling process. CO_2 is captured in the absorber at approximately 38 °C and is released from the regenerator at approximately121 °C at a much higher concentration.

In our investigation, the experimental apparatus consists of a packed-column absorber to promote

gas-liquid contact and reaction in a counter-current flow pattern. Figure 2 shows the schematic diagram of the packed column absorber. The glass absorber is 7.7-cm ID and packing height varied from 18-to 71-cm during this series of tests. It has an exterior jacket with hot water flowing in this outer jacket for absorber temperature control. The heat-jacketed section is 82.6-cm high. CO_2 absorbent enters from the top of the absorber through a spray nozzle to ensure good initial liquid distribution to the packing material. The spray nozzle, which delivers fine mists, is placed 1 inch above the packing. The liquid is electrically preheated to the reactor control temperature in the stainless steel inlet line. The baseline absorber temperature is normally set at 38 °C during CO_2 absorption. Liquid flow rate is controlled by a MicroMotion mass flowmeter. Flow rate data are continuously stored in a computer at a predetermined time interval.

Simulated flue gas enters from the bottom of the absorber. Gas flow rate is controlled by a mass flow meter controller manufactured by Tylan General. Gas flow rate data are also stored in computer files. The baseline gas composition is 15% CO_2 and 85% N_2. Sulfur oxides, hydrogen chloride, nitrogen oxides, and oxygen are not included in the simulated flue gas to avoid possible interferences with the test objectives for this series of experiments. These acid gases are known to cause degradation of the solvents. Coal-fired flue gas nominally consists of 15% CO_2 on a dry basis when the combustion takes place with 20% excess air.

The initial objectives of the experiments are: (1) to obtain first-hand data on the effect of structured packing versus traditional random (or dumped) packing on the CO_2 capture rate; (2) to obtain CO_2 capture rate data by monoethanolamine (MEA) and by a sterically hindered amine; and (3) to compare CO_2 stripping rates between CO_2 - rich MEA and CO_2 - rich sterically hindered amine. The sterically hindered amine used during this test series was 2-amino-2-methyl-1-propanol (AMP). AMP is a tertiary amine which reacts with CO_2 at a slower rate than MEA. Though AMP reacts with CO_2 at a slower rate, less energy is required to drive out CO_2 from its CO_2 - rich solution [1]. There is a wide selection of sterically hindered amines. Recently, in Japan, Kansei Electric Power Company, in conjunction with Mitsubishi Heavy Industries Limited, has developed a sterically hindered amine specifically for CO_2 recovery from flue gas [4]. TNO, in the Netherlands, also is developing liquid absorbents for flue gas applications [5]. However, the identities of those absorbents were not disclosed.

The basic reaction chemistry for monoethanolamine and CO_2 is represented by the following reversible reaction:

$$2\ RNH_2 + CO_2 \underset{\text{COLD}}{\overset{\text{HOT}}{\rightleftharpoons}} RNHCOO^- + RNH_3^+ \qquad [R = CH_2OH]$$

This is an exothermic reaction and 72 KJ of thermal energy is released per mole of CO_2 absorbed in MEA solution. Absorption usually takes place at 38 °C. During regeneration, more thermal energy (about 165 KJ/mole CO_2) is added to the solution to release the CO_2, because a large amount of water in the 20% by weight aqueous solution must be heated to regeneration temperature. Regeneration usually takes place at 121 °C. It has been estimated that up to 80% of total cost in the CO_2 absorption/regeneration cycle is due to the regeneration procedure.

Three types of column packings are compared for their CO_2 absorption rates at identical test conditions: Intalox saddle (ceramic, random packing), 1.9-cm and the smallest available from the supplier (Norton Chemical Process Products); Flexipac structured packing supplied by Koch Engineering Company; and BX Gauze structured packing also supplied by Koch Engineering Company. Structured packing provides more gas-liquid contact surface area per unit packed volume than random packings. Thus the overall CO_2 capturing capacity and rate by the liquid absorbent is increased. The packing height ranged approximately 18 cm to 71 cm during this series of tests.

CO_2 Absorption Rate Determination

Inlet nitrogen flow, inlet CO_2 concentration (vol%), and outlet CO_2 concentration (vol%) are used to calculate instantaneous absorption rates every 10 seconds during an absorption test. The nitrogen flow is measured by a mass flow controller. The inlet and outlet CO_2 concentrations are measured by an Horiba infrared gas analyzer, which is calibrated immediately before the test. The inlet CO_2 flow rate is calculated using the following equation:

$$G_i = [(F \times D/M)/(1 - y_i)]y_i \qquad (1)$$

where

G_i = CO_2 inlet flow rate, lb-mol/hr
F = nitrogen gas flow rate, ft^3/hr
D = density of nitrogen, lb/ft^3, at standard conditions
M = molecular weight of nitrogen
y_i = CO_2 mole fraction at inlet of absorber, vol%

The inlet CO_2 concentration, y_i, is averaged for the 20 data points (232 s) recorded immediately before solvent flow is initiated and is assumed constant throughout the test duration. The CO_2 inlet flowrate is controlled by a mass flow controller. The calculated flow rate, G_i, is used in the absorption calculation for data accuracy purposes. Since nitrogen gas is inert in the absorber, the outlet CO_2 flowrate is calculated using the nitrogen flow rate and outlet CO_2 concentration using the following equation:

$$G_o = [(F \times D/M)/(1 - y_o)]y_o \qquad (2)$$

where
G_o = CO_2 outlet flow rate, lb-mol/hr
y_o = CO_2 mole fraction at outlet of absorber, vol%

The CO_2 absorption rate is the difference between the inlet and outlet CO_2 flow rates. Total CO_2 absorbed in the absorber can be obtained by integrating the instantaneous rates over a selected time period. Efficiency of CO_2 absorption is defined as $[(y_i - y_o)/y_i] \times 100\%$ at steady state.

Regeneration

The CO_2 - rich liquid chemical absorbent can be regenerated by heating. CO_2 evolves from the rich liquid absorbent during the heating. This regenerated liquid absorbent is CO_2 - lean and recirculated to the absorber for reuse. The regeneration temperature is usually set at 121 °C under slightly elevated pressure in the carbon dioxide industry. In our investigation, the uniqueness of the laboratory regenerator is that the absorber was used as the regenerator during the regeneration phase of the absorption/regeneration cycle. The only difference is that higher temperature is maintained in the packed column in order to drive away CO_2 from the rich amine solution. The structured packing accelerates the CO_2 release from the CO_2 - rich amine solution. The CO_2 - rich solution, which is sprayed into the reactor, is trickling in a thin film down the extensive surface area provided by the packing. No purge gas is required during the regeneration; the recovered CO_2 is pure after condensing out the vapor. A bag meter is used to measure the total mass of CO_2 evolving from a known amount of CO_2 - rich amine solution; the time at every 2830 cm^3 (0.1 ft^3) advance at the bag meter is manually recorded.

RESULTS AND DISCUSSIONS

Absorber Efficiencies

Effects of absorbent (MEA) flow rate and packing type on CO_2 absorption efficiencies are compared. The test results are shown in Table 1. Higher absorbent flow rate increases CO_2 absorption efficiency as expected. Absorbent utilization is defined as efficiency divided by the stoichiometric ratio. Since it takes 2 moles of MEA to react with one mole of CO_2, the stoichiometric ratio for MEA is equal to the mole ratio divided by 2.

Three types of packings were studied for their effectiveness in CO_2 absorption: BX gauze, Flexipac, and random saddle (ceramic) packings. BX gauze and Flexipac structured packings are the products of Koch Engineering Company. At an absorbent to CO_2 mole ratio of 1.4, BX gauze improves packed column absorber efficiency by about 50% over the use of random saddle packing. Flexipac minimally improved efficiency over random saddle packing.

Comparison of CO_2 Absorption Rates

Table 2 shows that the sterically hindered amine, AMP, attained near equal CO_2 absorption rate using structured packing as compared to random saddle packing for MEA processing. In these tests, 29.2 wt% of AMP solution is used while only 20 wt% of MEA solution is used, because the molecular weight of AMP is larger than MEA. Thus equal mole concentration is maintained for both MEA and AMP in the absorbent solution, respectively. Flexipac structured packing did not significantly improve the CO_2 absorption rates.

Rate of CO_2 Regeneration: AMP vs MEA

To compare CO_2 regeneration rate between MEA and AMP, CO_2-saturated MEA and AMP solutions are prepared. The packed absorber, used as the regenerator, is only heated to 93 °C, since in the present reactor setup, this is the highest temperature that can be safely maintained to prevent the water or solution from boiling. CO_2 - saturated AMP or MEA solution is sprayed on the top of the packing, while the CO_2 releasing rate is recorded with the aid of a bagmeter. The data in Table 3 show that CO_2 releasing rate from AMP solution is about 80% faster than from MEA solution. No purge gas is used. The packed column has not been optimized, and a taller packed column is expected to improve the operation.

CONCLUSIONS

Investigations of amine-based scrubbing for CO_2 capture were performed to elucidate ways to improve this chemical absorption process. Increasing the gas-liquid contacting area has a major impact on scrubbing. Absorption tests revealed that for a particular amine, structured packing improves the absorber efficiency and absorption rate as compared to the more traditional random packing. The type of amine is also a consideration. At the same bed geometry, the conventional MEA performed much better during absorption studies than the sterically hindered amine, AMP. However, in the regeneration step, the CO_2 releasing rate from the saturated AMP solution is over 80% greater than from saturated MEA solution. By extracting information from the above results, it can be speculated that if the more easily-regenerable AMP is substituted for MEA, an overall process benefit will be obtained if a structured packing is used as compared to the random packing. Other techniques to improve the amine-based scrubbing will be investigated in the future.

DISCLAIMER

Reference in this report to any specific commercial process, product or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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TABLE 1
Absorber Efficiency and Absorbent/CO_2 Mole Ratio

Mole ratio	Efficiency, %	Packing	Utilization, %
1.4	61.3	BX gauze	87.6
1.4	60.9	BX gauze	87.0
1.4	62.2	BX gauze	88.8
2.2	97.2	BX gauze	88.4
2.3	98.9	BX gauze	86.0
1.4	41.4	Flexipac	59.1
1.4	40.1	random saddle	57.3

Absorbent: 20 wt% MEA — Absorber temp: 38 °C
Mole ratio: Mole absorbent inlet/mole CO_2 inlet — Absorber ht: 53 cm

TABLE 2
Packing Type and Absorbent Effects on CO_2 Absorption Rate

CO_2 Absorption Rate, kg-mol/s x 10^6	Absorbent	Packing
2.65	MEA	BX gauze
1.78	MEA	Random Saddle
1.88	AMP	BX gauze
1.23	AMP	Flexipac
1.15	AMP	Random Saddle

Absorbent: 20 wt% MEA Absorber temp: 38 °C
Absorbent: 29.2 wt% AMP Absorber ht: 53 cm
Mole Ratio: 1.4 (for both MEA and AMP)

TABLE 3
Rate of CO_2 Regeneration, AMP versus MEA

	MEA (20 wt%)	AMP (29.25 wt%)	CO_2 regeneration rate ratio AMP/MEA
CO_2 regeneration rate, kg-mol/s x 10^6	0.56	1.03	1.83
Regeneration temp °C	93	93	N/A
CO_2 saturated absorbent flow, lb/hr	10.7	10.7	NA

Structured packing ht: 53 cm (BX gauze)

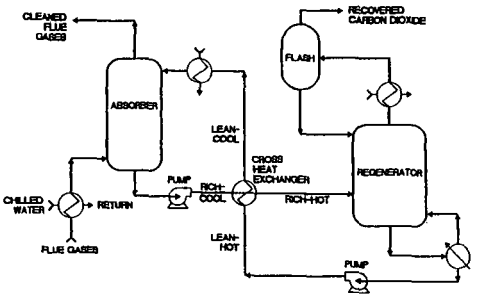

FIGURE 1. FLOWSHEET FOR THE RECOVERY OF CO_2 FROM FLUE GAS USING CHEMICAL ABSORPTION.

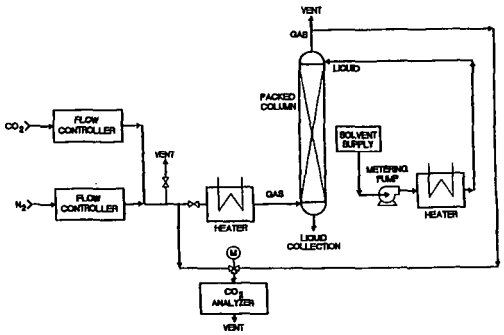

FIGURE 2. SIMPLIFIED FLOWSHEET FOR CO_2 SCRUBBING